

(12) PATENT APPLICATION
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 200197176 A1

(54) Title
Process for the hydrogenation of hydroformylation mixtures

(51)⁶ International Patent Classification(s)
C07C 029/141

(21) Application No: **200197176** (22) Application Date: **2001.12.11**

(30) Priority Data

(31) Number (32) Date (33) Country
10062448 2000.12.14 DE

(43) Publication Date : **2002.06.20**

(43) Publication Journal Date : **2002.06.20**

(71) Applicant(s)
Oxeno Olefinchemie GmbH

(72) Inventor(s)
Alfred Kaizik; Cord Knoop; Joachim Schuler; Dietmar Gubisch; Walter Toetsch; Wilfried Bueschken; Bernhard Scholz

(74) Agent/Attorney
SPRUSON and FERGUSON, GPO Box 3898, SYDNEY NSW 2001

BEST AVAILABLE COPY

PROCESS FOR THE HYDROGENATION OF HYDROFORMYLATION MIXTURES

Abstract:

The invention relates to a process for the hydrogenation of reaction mixtures from the hydroformylation of olefins having from 4 to 16 carbon atoms in the homogeneous liquid
5 phase over fixed-bed catalysts comprising at least one element of transition group eight of the Periodic Table of the Elements, wherein the homogeneous liquid phase of the output from the reactor still contains from 0.05 to 10% by weight of water.

10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
2206
2207
2208
2209
2210
2211
221

AUSTRALIA

PATENTS ACT 1990

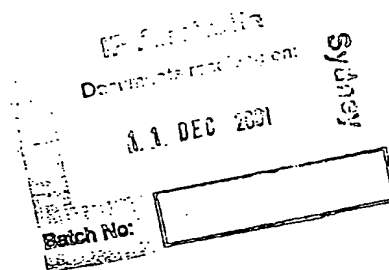
COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

Name and Address of Applicant :	Oxeno Olefinchemie GmbH Paul-Baumann-Strasse 1 D-45764 Marl Germany
Actual Inventor(s):	Alfred Kaizik Bernhard Scholz Wilfried Bueschken Walter Toetsch Dietmar Gubisch Joachim Schuler Cord Knoop
Address for Service:	Spruson & Ferguson St Martins Tower, Level 35 31 Market Street Sydney NSW 2000 (CCN 3710000177)
Invention Title:	Process For The Hydrogenation of Hydroformylation Mixtures

The following statement is a full description of this invention, including the best method of performing it known to me/us:-



Process for the hydrogenation of hydroformylation mixtures

The invention relates to a process for the hydrogenation of hydroformylation mixtures, i.e. for preparing alcohols by hydrogenation of aldehydes in the liquid phase in the presence of water.

Alcohols can be obtained by catalytic hydrogenation of aldehydes which have been obtained, for example, by hydroformylation of olefins. Large quantities of alcohols are used as solvents and as intermediates for preparing many organic compounds. Important downstream products of alcohols are plasticizers and detergents.

It is known that aldehydes can be catalytically reduced by means of hydrogen to form alcohols. Use is frequently made of catalysts which comprise at least one metal of groups 1b, 2b, 6b, 7b and/or 8 of the Periodic Table of the Elements. The hydrogenation of aldehydes can be carried out continuously or batchwise using pulverulent or palletized/shaped catalysts in the gas or liquid phase.

For the industrial production of alcohols by hydrogenation of aldehydes from the oxo process (hydroformylation of olefins), preference is given, especially in the case of large-volume products, to continuous gas- or liquid-phase processes using catalysts located in a fixed bed.

Compared to gas-phase hydrogenation, liquid-phase hydrogenation has a more favorable energy balance and gives a higher space-time yield. As the molar mass of the aldehyde to be hydrogenated increases, i.e. as the boiling point increases, the advantage of the more favorable energy balance increases. Higher aldehydes having more than 7 carbon atoms are therefore preferably hydrogenated in the liquid phase.

However, hydrogenation in the liquid phase has the disadvantage that, owing to the high concentrations of both aldehydes and alcohols, the formation of high boilers via subsequent and secondary reactions is promoted. Thus, aldehydes can more readily undergo aldol reactions (addition and/or condensation) and form hemiacetals or acetals with alcohols. The acetals formed can undergo elimination of water or alcohol to form enol ethers which are

hydrogenated under the reaction conditions to form the saturated ethers. These secondary by-products thus reduce the yield. The by-products referred to as high boilers can at best sometimes be redissociated in downstream plants to give products of value, e.g. starting aldehydes and target alcohols.

5

Industrial aldehyde mixtures which are used for the hydrogenation frequently already contain varying concentrations of high boilers.

10

Hydroformylation of olefins in the presence of cobalt catalysts gives crude aldehydes which contain esters of formic acid (formates) and also aldol products, high esters and ethers as well as acetals as high boilers. If these mixtures are hydrogenated in the gas phase, the major part of the high boilers can be separated off in the vaporizer and worked up in a separate process step to give products of value.

.....
.....
.....
.....
.....

15

In contrast, in the case of the liquid-phase hydrogenation, the high boilers remain in the reactor feed. They are mostly hydrogenated in the hydrogenation step, so that it is no longer possible to obtain a product of value from them.

.....
.....
.....

20

In US 5 059 710, the yield of alcohols in the hydrogenation of crude aldehydes is increased by redissociating part of the high boilers by means of water at elevated temperature to form aldehydes or alcohols in a process step upstream of the hydrogenation. Hydrolysis and hydrogenation are therefore separate process steps; nothing is said about the water content of the mixture to be hydrogenated.

.....
.....
.....

25

A similar process is disclosed in US 4 401 834. Here too, the cleavage of high boilers is carried out in the presence of water prior to the actual hydrogenation step.

30

GB 2 142 010 claims a process for the hydrogenation of crude aldehydes having from 6 to 20 carbon atoms which contain high boilers and small amounts of sulfur compounds to give the corresponding saturated alcohols. The hydrogenation is carried out in two reactors connected in series. The first reactor contains an MoS₂/C catalyst and the second reactor contains an Ni/Al₂O₃ catalyst. The hydrogenation in both reactors is carried out with addition of up to 10%

of water vapor, based on the feed stream, in a temperature range of from 180 to 260°C and a hydrogen partial pressure of from 150 to 210 bar using a large excess of hydrogen. In the examples, this is so large that the added water is present virtually only in the gas phase. The object of this process is to suppress the formation of hydrocarbons by hydrogenolysis of the alcohols. Nothing is said about an increase or decrease in high boilers and formates in the hydrogenation.

US 2 809 220 describes a liquid-phase hydrogenation of hydroformylation mixtures in the presence of water. The catalysts used are sulfur-containing catalysts. The hydrogenation is carried out in a pressure range of from 105 to 315 bar and a temperature range from 204 to 315°C in the presence of from 1 to 10% of water, based on starting material. To keep the added water in the gas phase, a large excess of hydrogen (from 892 to 3566 standard m3 of hydrogen per m3 of starting material) is used. As regards the high excess of hydrogen, reference is made to the discussion of GB 2 142 010. A further disadvantage of this process is the high specific energy consumption.

A further process for the hydrogenation of hydroformylation mixtures is disclosed in DE 198 42 370. This document describes the hydrogenation of hydroformylation mixtures in the liquid phase over copper-, nickel- and chromium-containing supported catalysts. Depending on the process used for preparing the hydroformylation mixtures (rhodium or cobalt processes), these mixtures contain water. The process disclosed is designed for the selective hydrogenation of the aldehydes to alcohols, without hydrogenation of the olefins which have remained unreacted in the hydroformylation, i.e. the high boilers (mostly acetals) are not converted into the useful product. This is economically unfavorable and is therefore capable of improvement.

Since the known processes are not optimal in respect of economics (low capital cost, high product yield and low energy consumption), it is an object of the invention to develop a new process for the hydrogenation of aldehydes or aldehyde mixtures to the corresponding saturated alcohols, which process combines the advantages of gas-phase hydrogenation (high selectivity) with those of liquid-phase hydrogenation (low energy consumption, high space-type yield).

It has been found that the yield of alcohols in the liquid-phase hydrogenation of aldehydes or industrial aldehyde mixtures is increased when the hydrogenation is carried out in the presence of water and the water is present mainly in the liquid phase under the reaction conditions and no separate liquid water phase is formed.

The invention accordingly provides a process for the continuous hydrogenation of reaction mixtures from the hydroformylation of olefins having from 4 to 16 carbon atoms in the homogeneous liquid phase over fixed-bed catalysts comprising at least one element of transition group eight of the Periodic Table of the Elements, wherein the homogeneous liquid phase of the output from the reactor still contains from 0.05 to 10% by weight of water and, in steady-state operation of the process, from 3 to 50% more hydrogen is fed in than is consumed by the hydrogenation.

The process of the invention has a series of advantages. In the hydrogenation of pure aldehydes in the liquid phase in the presence of homogeneously dissolved water, the yields and selectivities correspond to those of gas-phase hydrogenations, but the energy consumption is appreciably lower.

If aldehydes or aldehyde mixtures contain formates and high boilers, with the latter consisting predominantly of aldol products and acetals, are hydrogenated in the liquid phase in the presence of water, formates (formic acid esters) are converted virtually completely into alcohols and high boilers are partly converted into alcohols. As a result, the amount of alcohol formed is greater than the amount equivalent to the amount of aldehyde in the feed mixture.

In the hydrogenation of pure aldehydes or aldehydes low in high boilers by the process of the invention, high boiler formation in the hydrogenation is significantly reduced and the selectivity of the hydrogenation is improved significantly as a result. To obtain the selectivity- and yield-increasing action of the water, it is necessary for the water to be present in the liquid phase. The presence of water in the gas phase is therefore not decisive.

The starting materials for the preparation of the aldehydes or the reaction mixture by hydroformylation are olefins or mixtures of olefins having from 4 to 16, preferably from 6 to 12, carbon atoms and terminal or internal C-C double bonds, e.g. 1-butene, 2-butene, isobutene, 1- or 2-pentene, 2-methyl-1-butene, 2 methyl-2-butene, 3-methyl-1-butene, 1-, 2- or 3-
 5 hexene, the C6-olefin mixture obtained in the dimerization of propene (dipropene), heptenes, 2- or 3 methyl-1-hexene, octenes, 2-methylheptenes, 3-methylheptenes, 5-methyl-2-heptene, 6-methyl-2-heptene, 2-ethyl-1-hexene, the mixture of isomeric C8-olefins obtained in the dimerization of butenes (dibutene), nonenes, 2- or 3-methyloctenes, the C9-olefin mixture obtained in the trimerization of propene (tripropene), decenes, 2-ethyl-1-octene, dodecenes,
 10 the C12-olefin mixture obtained in the tetramerization of propene or the trimerization of butenes (tetrapropene or tributene), tetradecenes, pentadecenes, hexadecenes, the C16-olefin mixture obtained in the tetramerization of butenes (tetra-butene) and also olefin mixtures prepared by cooligomerization of olefins having different numbers of carbon atoms (preferably from 2 to 4), optionally after separation into fractions having an identical or similar chain
 15 length by distillation. It is likewise possible to use olefins or olefin mixtures produced by Fischer-Tropsch synthesis and also olefins obtained by oligomerization of ethene or olefins obtainable via methathesis reactions. Preferred starting materials for the preparation of the hydroformylation mixtures are C8-, C9-, C12-, C15- or C16-olefin mixtures.

20 The olefins are hydroformylated in a customary fashion and then represent the starting materials for the hydrogenation process of the invention. The hydroformylation is generally carried out using rhodium or cobalt catalysts with or without additives to stabilize the complex, e.g. organic phosphines or phosphites. The temperatures and pressures can, depending on the catalyst or olefin, be varied within wide limits. A description of the hydroformylation of
 25 olefins may be found, for example, in J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Heidelberg-New York, 1980, page 99 ff., and also in Kirk-Othmer, Encyclopedia of Chemical Technology, volume 17, 4th edition, John Wiley & Sons, pages 902 to 919 (1996).

30 In the process of the invention, preference is given to using hydroformylation mixtures prepared from C8-, C12-olefins or C8-, C12-olefin mixtures.

The amount of aldehyde in the feed to the reactor can be limited to concentrations of 1-35% by weight, preferably 5-20% by weight.

5 The reaction mixtures from the hydroformylation are advantageously firstly freed of the catalyst. If a cobalt catalyst has been used, this can be achieved by depressurization, oxidation of the cobalt carbonyl compounds remaining in the hydroformylation mixture in the presence of water or aqueous acid and separation of the aqueous phase. Cobalt removal processes are well known, cf., for example, J. Falbe, loc. cit., Kirk-Othmer, loc. cit., 164, 175, BASF process.

10

If a rhodium compound is used as hydroformylation catalyst, it can, for example, be separated off as distillation residue by means of thin film evaporation.

.....
.....
.....
.....

15

The reaction mixtures from the cobalt-catalyzed hydroformylation which have been freed of the hydroformylation catalyst generally comprise from 3 to 40% by mass, usually from 5 to 30% by mass, of low boilers, mainly unreacted olefins, together with the corresponding saturated hydrocarbons and also from 0.05 to 5% by mass of water, from 30 to 90% by mass of aldehydes, from 5 to 60% by mass of alcohols, up to 10% by mass of formates of these alcohols and from 3 to 15% by mass of high boilers.

.....
.....

20

20

In contrast to the cobalt-catalyzed hydroformylation, the reaction mixtures from the rhodium-catalyzed hydroformylation contain virtually no water. In this case, water has to be introduced in appropriate amounts.

.....
.....

25 However, it must be emphasized that the process of the invention can also be carried out using hydroformylation mixtures whose composition does not correspond to that indicated above in this or any other respect. Thus, for example, the hydrocarbons (olefins and paraffins) can be separated off from the hydroformylation mixture prior to the hydrogenation.

30 The hydrogenation of aldehydes by means of the process of the invention in the liquid phase in the presence of water can be carried out using palletized/shaped catalysts located in a fixed bed. These may comprise one or more metals of groups 1b, 2b, 6b, 7b and/or 8 of the

Periodic Table, in particular nickel, copper and chromium. It is possible to use catalysts on oxidic supports such as aluminum oxide, silicon oxide, titanium oxide, aluminosilicates or support-free catalysts. Support-free catalysts generally comprise from about 0.2 to 30% by weight of nickel, from 0.3 to 40% by mass of copper and from 18 to 40% by mass of chromium. The catalysts can further comprise up to 20% by mass of basic substances such as alkali metal or alkaline earth metal oxides or hydroxides, and also other inert or property-modifying materials in the same amounts, for example graphite. The catalysts used according to the invention do not contain any sulfur or sulfur compounds.

Preferred catalysts in the process of the invention for the hydrogenation of aldehydes to alcohols are supported catalysts. The catalysts contain from 0.3 to 15% by weight of copper and from 0.3 to 15% by weight of nickel and also, as activators, from 0.05 to 3.5% by weight of chromium and advantageously from 0 to 1.6% by weight of an alkali metal. The support material preferably comprises aluminum oxide and/or silicon oxide.

The catalysts are advantageously used in a form in which they offer a low flow resistance, e.g. in the form of granules, pellets or shaped bodies such as tablets, cylinders, spheres, extrudates or rings. They are advantageously activated prior to use by heating in a stream of hydrogen at, for example, from 140 to 250°C if they are not reduced in the hydrogenation reactor. For example, a method of reduction by means of hydrogen in the presence of a liquid phase is described in DE 199 33 348.3.

According to the invention, the hydrogenation is carried out in the homogeneous liquid phase in the presence of water, with the homogeneous liquid phase of the output from the reactor containing from 0.05 to 10% by weight, preferably from 0.5 to 8% by weight, particularly preferably from 1 to 5% by weight, of water. The stated water contents are to be regarded as independent of consumption of water by chemical reactions and of discharge of water together with the offgas from the hydrogenation. Under the reaction conditions of the hydrogenation, the water is present mainly in the organic starting material/product phase and only a small proportion is present in the gas phase. In the ideal case, no water is present in the gas phase. A further, liquid water phase is not present. The specific amount of water in the organic phase is determined by the solubility of water, the vapor pressure of water and the

phase ratio (gas to liquid) under the reaction conditions. The minimum amount of water necessary is that which is consumed in the hydrolysis of formic acid esters, acetals, enol ethers, aldol condensation products and any other hydrolyzable substances. If the starting material contains large proportions of hydrolyzable compounds, it may be necessary to add only part of the required water at the beginning in order to prevent formation of a second aqueous phase in the hydrogenation reactor. The other part is fed in during the hydrogenation as a function of the water consumption. When using only one reactor, this may be carried out at one or more points on the reactor; when using a plurality of reactors connected in series, advantageously before the individual reactors. To prevent any aldehyde protected as hemiacetal or acetal from escaping hydrogenation, the output from the hydrogenation (in the case of a plurality of reactors, from the last reactor) may still contain water. The water content of the homogeneous liquid phase of the output from the reactor can be from 0.05 to 10% by mass, preferably from 0.5 to 8% by mass.

Various process variants can be chosen for the process of the invention. It can be carried out adiabatically or virtually isothermally, i.e. with a temperature increase of less than 10°C, in one or more stages. In the latter case, all reactors, advantageously tube reactors, are operated adiabatically or virtually isothermally or one or more are operated adiabatically and the others are operated virtually isothermally. It is also possible for the aldehydes or aldehyde mixtures to be hydrogenated in the presence of water in a single pass or with product recirculation.

The process of the invention is carried out in cocurrent in the trickle phase or preferably in the liquid phase in three-phase reactors, and the hydrogen is finely dispersed in the liquid aldehyde stream in a manner known per se. In the interests of uniform liquid distribution, improved removal of heat of reaction and a high space-time yield, the reactors are preferably operated as high liquid throughputs of from 15 to 120 m³, in particular from 25 to 80 m³, per m² of cross section of the empty reactor an hour. If a reactor is operated isothermally and in a single pass, the space velocity over the catalyst (LHSV) can be from 0.1 to 10 h⁻¹.

In the hydrogenation of hydroformylation mixtures having from 8 to 17 carbon atoms, for example isononanal or tridecanal, preference is given to using a plurality of reactors

connected in series. In this case, the first reactor is operated in the recirculation mode and the subsequent reactor(s) is(are) operated in the recirculation mode or in a single pass. As a reactor operated in the recirculation mode, it is possible to use, for example, a shaft oven with a heat exchanger in an external circuit or a shell-and-tube reactor.

5

To minimize secondary reactions and thus to increase the alcohol yield, it is advantageous to limit the aldehyde concentration in the feed to the reactor. Particularly in the hydrogenation of hydroformylation mixtures having from 8 to 17 carbon atoms, the aldehyde content in the reactor feed is from 1 to 35%, preferably from 5 to 25%. In the case of reactors operated in the recirculation mode, a concentration in the desired range can be set by means of the
 10 recirculation ratio (ratio of recirculated hydrogen
 ation product to feed).

•••••
•••••

•••••
•••••

••••• 15

The process of the invention is carried out in a pressure range from 5 to 100 bar, in particular from 5 to 40 bar, particularly preferably in the range from 10 to 25 bar. The hydrogenation temperatures are in the range from 120 to 220°C, in particular from 140 to 190°C.

•••••
•••••

•••••
•••••

••••• 20

The hydrogen necessary for the hydrogenation is preferably used in pure form in only a small excess, so that little water goes into the gas phase and is carried out with the latter. The amount of hydrogen fed into each reactor is from 103 to 150% of the amount consumed by reaction, in particular from 103 to 120%. In other words, the hydrogen consumed in the hydrogenation is replaced in an excess of from 3 to 50%, preferably from 3 to 20%, particularly preferably from 5 to 10%.

•••••
•••••

25 The hydrogenation product is worked up by distillation. This is carried out at atmospheric pressure or under reduced pressure. In the case of high-boiling alcohols, distillation under reduced pressure is preferred.

30 The following examples illustrate the invention but do not restrict its scope which is defined by the claims.

Example 1 (comparative example):

C9-Aldehyde hydrogenation in the liquid phase/water-free crude aldehyde as starting material

One liter of crude reaction product from the Co-catalyzed hydroformylation of dibutene containing 1.15% by weight of water and 5.16% by weight of high boilers was subjected to a laboratory distillation to remove the water (down to 110 ppm of residual water) and then hydrogenated in the liquid phase in a circulation apparatus at 180°C and 25 bar absolute over 100 g of a Cu/Cr/Ni catalyst on an Al₂O₃ support. The amount of offgas was 1 standard l/h. The analyses of starting material and product are shown in table 1.

Table 1:

Running time (hours)	C8-hydrocarbon (% by weight)	C9-aldehyde (% by weight)	Formate (% by weight)	C9-alcohol (% by weight)	High boilers (% by weight)
0	9,32	46,50	3,24	35,79	5,16
1	9,28	0,29	1,35	83,64	5,44
2	9,25	0,18	0,45	84,03	6,10
3	9,18	0,15	0,22	84,00	6,45

As can be seen from table 1, the high boilers are not cleaved, but are instead formed, when the hydrogenation of isononanal is carried out in the absence of water in the starting material.

Example 2 (according to the invention):

C9-Aldehyde hydrogenation/water-containing crude aldehyde as starting material

One liter of crude reaction product from the Co-catalyzed hydroformylation of dibutene containing 1.5% by weight of residual water and 5.35% by weight of high boilers was hydrogenated in the liquid phase in a circulation apparatus at 180°C and 25 bar absolute over

100 g of a Cu/Cr/Ni catalyst on an Al₂O₃ support. The amount of offgas was 1 standard l/h. The analyses of starting material and product are shown in table 2, calculated on an anhydrous basis.

5 Table 2:

Running time (hours)	C8-hydro carbon (% by weight)	C9-alde hyde (% by weight)	Formate (% by weight)	C9-alcohol (% by weight)	High boilers (% by weight)
0	9,12	47,2	3,16	37,17	5,35
1	9,18	0,34	0,32	85,72	4,45
2	9,15	0,20	< 0,01	86,67	3,84
3	9,09	0,18	< 0,01	86,86	3,73

As can be seen from table 2, part of the high boilers is cleaved to form products of value during the hydrogenation of crude isononanal in the presence of water in the starting material and the formates are reacted more rapidly and virtually quantitatively. After the hydrogenation, the liquid reaction mixture contains 1.01% by weight of water.

15 Example 3 (according to the invention):

C9-Aldehyde hydrogenation/water-containing starting material low in high boilers

One liter of crude reaction product from the Co-catalyzed hydroformylation of dibutene containing 1.20% by weight of water was subjected to a laboratory distillation to substantially remove the high boilers (from 4.65% by weight down to 0.13% by weight) and then hydrogenated in the liquid phase in a circulation apparatus at 180°C and 25 bar absolute over 100 g of a Cu/Cr/Ni catalyst on an Al₂O₃ support. The amount of offgas was 1 standard l/h. The analyses of starting material and product are shown in table 3.

Table 3:

Running time (hours)	C8-hydro carbon (% by weight)	C9-alde hyde (% by weight)	Formate (% by weight)	C9-alcohol (% by weight)	High boilers (% by weight)
0	7,40	52,86	3,44	36,17	0,13
1	7,27	0,26	0,18	90,83	1,46
2	7,29	0,21	0,01	90,87	1,48
3	7,32	0,19	<0,01	90,86	1,49

As can be seen from table 3, the isononyl formates are very quickly converted into the desired product isononanol in the hydrogenation of isononanal in the presence of water dissolved homogeneously in the starting material.

The high boiler contents settle down to a constant value of about 1.46% by weight after a running time of one hour.

After the hydrogenation, the reaction mixture contains 0.70% by weight of water.

Example 4 (comparison):

C9-Aldehyde hydrogenation/water-free starting material low in high boilers

One liter of crude reaction product from the Co-catalyzed hydroformylation of dibutene was subjected to a laboratory distillation to remove the residual water (from 1% by weight to 150 ppm) and high boilers and hydrogenated in the liquid phase in a circulation apparatus at 180°C and 25 bar absolute over 100 g of a Cu/Cr/Ni catalyst on an Al₂O₃ support. The amount of offgas was 1 standard l/h. The analyses of starting material and product are shown in table 4.

Table 4:

Running time (hours)	C8-hydro carbon (% by weight)	C9-alde hyde. (% by weight)	Formate (% by weight)	C9-alcohol (% by weight)	High boilers (% by weight)
0	6,95	51,50	3,64	37,79	0,13
1	6,97	0,33	1,21	87,05	4,44
2	6,98	0,19	0,50	89,21	3,13
3	6,94	0,15	0,27	89,63	3,01

As can be seen from table 4, the isononyl formates are, in contrast to example 3, converted only slowly into the desired product isononanol in the hydrogenation of isononanal in the absence of water in the starting material. Furthermore, high boiler formation is significantly higher in the absence of water.

The claims defining the invention are as follows:

1. A process for the continuous hydrogenation of reaction mixtures from the hydroformylation of olefins having from 4 to 16 carbon atoms in the homogeneous liquid phase over fixed-bed catalysts comprising at least one element of transition group eight of the periodic Table of the Elements, wherein the homogeneous liquid phase of the output from the reactor still contains from 0.05 to 10% by weight of water and, in steady-state operation of the process, from 3 to 50% more hydrogen is fed in than is consumed by the hydrogenation.
2. The process as claimed in claim 1, wherein the homogeneous liquid phase of the output from the reactor contains from 0.5 to 8% by weight of water.
3. The process as claimed in claim 1 or claim 2, wherein the homogeneous liquid phase of the output from the reactor contains from 1 to 5% by weight of water.
4. The process as claimed in any one of claims 1 to 3, wherein the hydrogenation is carried out at a pressure of from 5 to 100 bar.
5. The process as claimed in claim 4 wherein the pressure is from 5 to 40 bar.
6. The process as claimed in any one of claims 1 to 5, wherein the hydrogenation is carried out at a temperature of from 120 to 220°C.
7. The process as claimed in any one of claims 1 to 6, wherein catalysts comprising two metals selected from the group consisting of copper, chromium and nickel are used.
8. The process as claimed in any one of claims 1 to 6, wherein catalysts comprising copper, chromium and nickel are used.
9. The process as claimed in claim 8, wherein the fixed-bed catalyst comprises from 0.3 to 15% by weight of copper, from 0.3 to 15% by weight of nickel, from 0.05 to 3.5% by weight of chromium and from 0 to 1.6% by weight of an alkali metal.
10. The process as claimed in any one of claims 1 to 9, wherein the fixed-bed catalyst comprises silicon dioxide and/or aluminum oxide as support material.
11. The process as claimed in any one of claims 1 to 10, wherein the aldehyde concentration in the feed to the reactor is from 1 to 35%.
12. The process as claimed in any one of claims 1 to 11, wherein the aldehyde concentration in the feed to the reactor is from 5 to 20%.
13. The process as claimed in any one of claims 1 to 12, wherein hydroformylation mixtures prepared from C8-olefins or C8-olefin mixtures are used.
14. The process as claimed in any one of claims 1 to 12, wherein hydroformylation mixtures prepared from C12-olefins or C12-olefin mixtures are used.
15. A process for the continuous hydrogenation of reaction mixtures from the hydroformylation of olefins having from 4 to 16 carbon atoms in the homogeneous liquid phase over fixed-bed catalysts comprising at least one element of transition group eight of

the periodic Table of the Elements, said process being substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

16. A C_{2-16} alcohol produced by the process of any one of claims 1 to 15.

Dated 2 November, 2001

Oxeno Olefinchemie GmbH

Patent Attorneys for the Applicant/Nominated Person

SPRUSON & FERGUSON

20
21
22
23
24

25
26

27
28

29
30

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

